

# PATENT SPECIFICATION

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## (54) DETERGENT COMPOSITIONS CONTAINING PARTICLE-DEPOSITION-ENHANCING AGENTS

(71) We, THE PROCTER & GAMBLE COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to detergent compositions. Such compositions include shampoos (liquid and cream), laundering hard surface and dishwashing detergents (granular and liquid) and personal use toilet bars which contain a water-insoluble or sparingly soluble particulate substance which is capable of imparting a desired residual property to a surface to which it becomes affixed.

British Patent Specification No. 1,111,708, discloses and claims a detergent composition comprising an organic surfactant, a water-soluble cationic polymer which is a polyethylenimine or alkoxyated polyethylenimine having molecular weight greater than 200, and a particulate heavy metal salt of 2-pyridinethiol-1-oxide. The cationic polymer has the effect of enhancing deposition and retention of the particulate heavy metal salts of 2-pyridinethiol-1-oxide on surfaces which are washed with the compositions of that invention.

The present invention is an improvement in or modification of the invention of No. 1,111,708.

It has now been found that certain of the cationic polymers of the above patent are also capable of enhancing deposition and retention of water-insoluble or sparingly soluble particulate substances, other than heavy metal salts of 2-pyridinethiol on surfaces which are washed with a detergent composition contain-

ing the cationic polymer and the water-soluble or sparingly soluble particulate substance. The invention provides a detergent composition comprising:

- (1) an organic surfactant,
- (2) a water soluble cationic polymer which is a polyethylenimine having a molecular weight in the range 2,000 to 3,000,000 or a reaction product of polyethylenimine with ethylene oxide and/or propylene oxide, the reaction product having a molecular weight of 30,000 to 1,000,000 and a weight ratio of polyethylenimine to alkylene oxide of at least 1:1,
- (3) a water-insoluble or sparingly soluble particulate substance, other than a heavy metal salt of 2-pyridinethiol-1-oxide, which is capable of imparting a desired residual property to a surface to which it becomes affixed when the surface is washed with the detergent composition.

Various water-insoluble particulate substances have been incorporated in detergent products for the purpose of imparting some residual property or characteristics on surfaces washed with the products. For example, shampoo compositions containing particulate antidandruff agents have been developed which function by deposition and retention of the particulate agent on the hair and scalp during shampooing. Sufficient quantities of the deposited particulate agents are retained after rinsing to impart some degree of residual antimicrobial activity to the washed hair and scalp. Such antidandruff shampoo compositions are disclosed, for example, in British Specification No. 957,458.

Particulate antimicrobial substances have also been used in various laundry detergents and personal use toilet detergent bars to im-

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part residual antimicrobial activity on the fabrics or skin surfaces washed with same. Such products are disclosed by Reller and Jordan in U.S. Patents 3,134,711, granted May 26, 1964 and 3,256,200, granted in June 14, 1966.

Various other water-insoluble or sparingly soluble particulate materials such as substances which absorb ultraviolet light (i.e. sunscreens), fabric brighteners, and whiteners have been employed in detergent compositions and depend for their activity on particulate deposition and retention on washed surfaces.

It is apparent that an effective detergent composition, properly used, will by its very nature tend to minimize retention of particulate matter on washed surfaces. Thus, only a relatively small portion of particles present in such detergent compositions are actually retained after rinsing of the washed surface. Since the activity of antimicrobial and other particulate agents is in part a function of the quantity of particles deposited and retained on the involved surfaces, measures which enhance deposition and/or promote retention of such particles serve to reduce the quantity of the substance in the composition required to attain a given level of activity or increase the activity attainable with a given concentration of such particles.

It has now been discovered that polyethylenimine and alkoxyated polyethylenimine polymers, as defined above, enhance the deposition and retention of water-insoluble or sparingly soluble particulate substances contained in detergent compositions, on surfaces washed therewith.

Although the mechanism whereby this phenomenon occurs is not fully understood, it is believed that the polymer coats or attaches itself in some way on the involved particles imparting a net positive charge thereto which increases the affinity of the particle for the generally negatively charged washed surfaces.

Organic surfactants (surface active agents i.e. detergent compounds) which can be used in the compositions of this invention are anionic, ampholytic, polar nonionic, nonionic, zwitterionic or cationic. The surfactant can form from 2 to 95% by weight of the total composition. Anionic organic surfactants are generally preferred for the purposes of this invention. Suitable anionic surfactants include the water-soluble salts of organic sulfuric reaction products having in their molecular structure an alkyl group containing from 8 to 20 carbon atoms and a sulfonic acid or sulfuric acid ester radical. Such surfactants include the sodium, potassium, and triethanolamine alkyl sulfates, especially those derived by sulfation of higher alcohols produced by reduction of tallow or coconut oil glycerides; sodium or potassium alkyl ben-

zene sulfonates, especially those of the types described in British Patent Specification No. 645,129 in which the alkyl group contains from 9 to 15 carbon atoms; sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols obtained from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium salts of sulfuric acid esters of the reaction product of one mole of a higher alcohol (i.e., tallow or coconut oil alcohols) and about 3 moles of ethylene oxide; and the water-soluble salts of condensation products of fatty acids with sarcosine, e.g., triethanolamine N-acyl sarcosinate, the acyl radicals being derived from coconut oil fatty acids and preferably containing 10 to 18 carbon atoms.

Preferably, anionic organic surfactants of the high sudsing type are used for the shampoo embodiments of this invention. Thus, alkyl glycerol ether sulfonates, N-acyl sarcosinates, and alkyl ether ethylene oxide sulfates as described above are used to special advantage. These and the foregoing surfactants can be used in the form of their sodium, potassium or lower alkanol-amine (e.g., mono-, di-, and triethanolamine) salts.

Conventional soaps may also be used as anionic surfactants for the purposes of this invention. Suitable soaps include the water-soluble salts, e.g., sodium, potassium, and lower alkanol-amine salts of higher fatty acids occurring in coconut oil, soybean oil, castor oil or tallow, or synthetically produced fatty acids may be used.

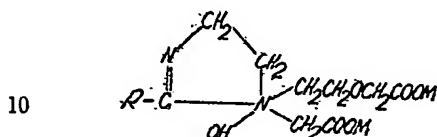
Polar nonionic surfactants can be used herein, either alone or in admixture with anionic and/or ampholytic surfactants. Surfactants of this class can serve to enhance lathering and cleaning properties of anionic detergents. By "polar nonionic surfactant" is meant a surfactant in which the hydrophilic group contains a semi-polar bond e.g.,  $N \rightarrow O$ ,  $P \rightarrow O$ ,  $As \rightarrow O$ , and  $S \rightarrow O$ . (The arrow is the conventional representation of a semi-polar bond). There is charge separation between the two bonded atoms, but the surfactant molecular bears no net charge and does not dissociate into ions.

A preferred polar nonionic surfactant for use in the present compositions is an amine oxide of the general formula  $R_1R_2R_3N \rightarrow O$ , wherein  $R_1$  is an alkyl, alkenyl, or monohydroxy-alkyl radical having from 10 to 16 carbon atoms, and  $R_2$  and  $R_3$  are each methyl, ethyl, propyl, ethanol or propanol radicals. An especially preferred amine oxide is dodecyl dimethylamine oxide.

Other operable polar nonionic surfactants are the phosphine oxides having the general formula  $R_1R_2R_3P \rightarrow O$ , wherein  $R_1$  is an alkyl, alkenyl or monohydroxyalkyl radical ranging in chain length from 10 to 18 carbons, and  $R_2$  and  $R_3$  are each alkyl or mono-

hydroxyalkyl radicals containing from 1 to 3 carbon atoms. A preferred phosphine oxide is dodecyldimethyl phosphine oxide.

- 5 Suitable amphoteric surfactants include the alkyl beta-iminodipropionates,  $RN(C_2H_5COOM)_2$ ; alkyl beta-aminopropionates  $RN(H)C_2H_5COOM$ ; and long chain imidazole derivatives having the general formula:



- In each of the above formulae, R is an acyclic hydrophobic group containing from 8 to 18 carbon atoms and M is a cation to neutralize the charge of the anion, e.g., an alkali metal cation such as sodium, potassium or ammonium or substituted ammonium cations. Specific useful amphoteric surfactants include the disodium salt of lauroyl-cycloimidinium - 1 - ethoxy - ethionic acid - 2-ethionic acid, dodecyl beta-alanine, and the inner salt of 2-trimethylamino lauric acid. As zwitterionics, the substituted betaines such as alkyl dimethyl ammonio acetates wherein the alkyl radical contains from about 12 to about 18 carbon atoms can also be used. Several examples of this class of zwitterionic surfactants are set forth in Canadian Patent 696,355.

- Especially preferred shampoo compositions in accordance with this invention will contain a non-soap anionic organic surfactant at a concentration of from about 8% to about 30% by weight of the total composition.

- Although nonionic and cationic surfactants are not usually preferred for the purposes of this invention they can nevertheless be used without substantial loss of the advantageous effects of the cationic polymers on deposition and retention of particulate matter on washed surfaces. Nonionic surfactants may be described as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. As those skilled in the art are well aware, the length of the hydrophilic or polyoxyalkylene radical required for condensation with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

- For example, a well known class of nonionics is made available on the market under the tradename of "Pluronic". These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propy-

lene glycol. The hydrophobic portion of the molecule, of course, exhibits water insolubility. The molecular weight of this portion is of the order of 950 to 4,000. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole. Liquid products are obtained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

Suitable nonionics also include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having 6 to 12 carbon atoms, either straight chain or branched chain, in the alkyl group with ethylene oxide in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.

Other suitable nonionics may be derived by the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. Here again, a series of compounds may be produced, depending on the desired balance between hydrophobic and hydrophilic elements. For example, compounds (molecular weight from 5,000 to 11,000) of 40 to 80% polyoxyethylene content and resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 to 3,000 are satisfactory.

Further satisfactory nonionics include the condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, either straight chain or branched chain, with ethylene oxide, an example being a coconut alcohol/ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

Cationic surfactants which can be used in the compositions of this invention include distearyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, coconut alkyl dimethyl benzyl ammonium chloride, dicoconut alkyl dimethyl ammonium chloride, cetyl pyridinium chloride, and cetyl trimethyl ammonium bromide.

As hereinbefore stated, the compositions of this invention contain as an essential component a water-soluble cationic polyethylenimine of molecular weight 2,000 to 3,000,000 or a reaction product of polyethylenimine with ethylene oxide and/or propylene oxide, the reaction product having molecular weight 30,000 to 1,000,000 and a weight ratio of polyethylenimine to alkylene oxide of at least 1:1.

It is believed that the structural formula of the backbone of polyethylenimine is:



wherein X represents a whole number of sufficient magnitude to yield a polymer of molecular weight of 2,000 to 3,000,000. Branch chains occur along the polymeric backbone and the relative proportions of primary, secondary and tertiary amino groups present on the polymer will vary, depending on the manner of preparation. The distribution of amino groups in a typical polyethylenimine is approximately as follows:

	$\text{CH}_2\text{—CH}_2\text{—NH}_2$	30%
15	$\text{CH}_2\text{—CH}_2\text{—NH}$	40%
	$\text{CH}_2\text{—CH}_2\text{—N—}$	30%

The polyethylenimine is characterized herein in terms of molecular weight. Such polymers can be prepared, for example, by polymerizing ethylenimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods are described in U.S. Patent Nos. 2,182,306, 3,033,746, 2,208,095, 2,806,839 and 2,553,696. Preferably, the polyethylenimine has a molecular weight of 30,000 to 1,000,000.

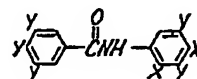
Alkoxyated polyethylenimine can be prepared, for example, by reacting one part by weight of ethylene oxide or propylene oxide with one part by weight of polyethylenimine prepared as described above. The weight ratio of polyethylenimine to alkylene oxide should be at least 1:1 for the purpose of this invention. A preferred ethoxyated polyethylenimine has a molecular weight of 80,000 to 120,000 and a weight ratio of polyethylenimine to ethylene oxide of at least 1:1.

The cationic polymer can be employed herein at a concentration within the range from 0.1 to 10.0% by weight, preferably from 0.25 to 4.0% by weight.

Particulate substances which can be used in the detergent compositions of this invention preferably have an average particle diameter within the range from 0.2 to 50 microns and include water-insoluble or sparingly soluble anti-microbial agents, sunscreens, fabric brighteners, and various substances which create a favorable skin feel after washing. These particulate substances depend on deposition and retention on washed surfaces to produce their intended effect.

Particulate antimicrobial substances, the deposition and retention of which is enhanced by the cationic polymers described herein include, for example

(a) substituted salicylanilides having the general formula:



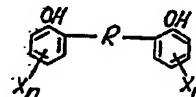
wherein X is hydrogen or halogen, and Y is hydrogen, halogen or trifluoromethyl;

(b) substituted carbanilides having the general structural formula:



wherein Y is hydrogen, halogen, or trifluoromethyl, X<sub>1</sub> is halogen or ethoxy, X<sub>2</sub> is hydrogen or halogen;

(c) substituted bisphenols having the general structural formula:



wherein X is a halogen and n is an integer from 1 to 3, R is an alkylene radical having from 1 to 4 carbon atoms or divalent sulfur, and

(d) mixtures of (a), (b), and (c).

The salicylanilides encompassed by (a) above include 3,4,5 - tribromosalicylanilide; 5 - bromosalicyl - 3,5 - di(trifluoromethyl) - anilide; 5 - chlorosalicyl - 3,5 - di(trifluoromethyl)anilide; 3,5 - dichlorosalicyl - 3,4 - dichloranilide; and 5 - chlorosalicyl - 3 - trifluoromethyl - 4 - chloranilide. These and other salicylanilides useful herein are disclosed in British Patent Specification 745,607.

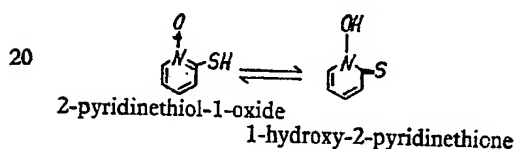
The preferred carbanilides of (b) above include 3,4,4' - trichlorocarbanilide; 3 - trifluoromethyl - 4,4' - dichlorocarbanilide; 3 - trifluoromethyl - 3',4,4' - trichlorocarbanilide; 3,3' - bis(trifluoromethyl - 4 - ethoxy - 4' - chlorocarbanilide; and 3,5 - bis(trifluoromethyl)-4-chlorocarbanilide.

The compounds in (c) above in which R represents an alkylene radical are more fully described in British Patent Specification No. 545,648. The preferred compounds of the general class of (c) above are those with symmetrical structures such as bis(5-chloro-

2 - hydroxyphenyl) methone, bis(3,5 - di - chloro - 2 - hydroxyphenyl)methane, bis - (3,5,6 - trichloro - 2 - hydroxyphenyl) - methane, bis(3,5 - dichloro - 2 - hydroxy - phenyl)sulfide, bis(3,5,6 - trichloro - 2 - hydroxyphenyl)sulfide, and mixtures thereof.

Additional antimicrobial compounds suitable for use in this invention are N-trichloromethylmercapto - 4 - cyclohexene - 1,2 - dicarboximide and N - (1,1,2,2 - tetrachloro - ethylsulfenyl) - cis -  $\Delta$  - 4 - cyclohexene - 1,2-dicarboximide.

In addition to the bacterial agents described above there may advantageously be included in the present compositions salts of 2-pyridinethiol-1-oxide which has the following structural formula in tautomeric form, the sulphur being attached to the 2-position of the pyridine ring:



Heavy metal salts of the above compounds are sparingly soluble and have a high degree of antibacterial activity. Preferred salts include zinc, cadmium, tin and zirconium 2-pyridinethiol-1-oxide.

Combinations of the above-described antibacterial substances can be used to advantage. Such combinations are disclosed in U.S. Patent 3,281,366.

These antimicrobial compounds are used in particulate form, with average particle sizes ranging from about 0.2 to about 30 microns. The quantity of antimicrobial agent employed can range from 0.1 to 10% and preferably from 0.5 to 2% by weight of the composition.

Preferred antimicrobial detergent compositions in accordance with this invention especially adapted to washing hair and scalp comprise from 10 to 35% by weight of at least one nonionic, ampholytic or zwitterionic surfactant; from 0.25 to 2.0% by weight of a polyethylenimine or alkoxyated polyethylenimine polymer having an average molecular weight within the range from 30,000 to 1,000,000 and having a weight ratio of polyethylenimine to alkylene oxide of at least 1:1, from 0.5 to 2.0% by weight of a water-insoluble or sparingly soluble antimicrobial substance in particulate form; the balance being substantially water.

Detergent compositions in accordance with this invention can be prepared by methods well known in the art; however, it has been found that especially good results are obtained when the cationic polymer and particulate substances are uniformly admixed in an initial step, with the mixture then being

added to an aqueous solution or slurry of the surfactant. If the polymeric component and particulate substances are added to the surfactant separately, the degree of deposition and retention enhancement effected by the polymer will be somewhat less.

Each of the above components can be incorporated in an aqueous vehicle which may, in addition, include such materials as organic solvents, such as ethanol; thickeners, such as carboxymethylcellulose, magnesium - alu - minium silicate, hydroxyethylcellulose or methylcellulose; perfumes, sequestering agents, such as tetrasodium ethylenediamine-tetracetate; and opacifiers, such as zinc stearate or magnesium stearate, which are useful in enhancing the appearance or cosmetic properties of the product.

Coconut acyl mono- or diethanol amides as suds boosters, and strongly ionizing salts such as sodium chloride and sodium sulfate may also be advantageously used.

Toilet detergent or soap bars containing a cationic polymer and particulate substance according to this invention can be based on soap or non-soap synthetic detergents and can also contain a variety of adjuvants to improve product performance or appearance. Examples of such adjuvants include free fatty acids or cold cream to improve cosmetic properties, perfumes, inorganic salts to improve bar firmness, insoluble soap to improve bar texture, coloring matter and the like.

In the case of heavy-duty laundering detergents containing the cationic polymers and particulate substances in accordance with this invention, such detergents can be in granular, flake, liquid or tablet form and can contain, in addition to detergent and inorganic or organic builder compounds (such as those disclosed in British Patent Specification No. 1,035,913), minor amounts of adjuvant materials which make the product more effective or more attractive. The following are mentioned by way of example. A tarnish inhibitor such as benzotriazole or ethylenethiourea may also be added in amounts up to about 2%. Fluorescers, perfume and color while not essential in the compositions of the invention, can be added in amounts up to about 1%. An alkaline material or alkali, such as sodium hydroxide or potassium hydroxide, can be added in minor amounts as supplementary pH adjusters when needed. Other suitable additives include brightening agents, sodium sulfate and sodium carbonate.

Corrosion inhibitors generally are also added. Soluble silicates are highly effective inhibitors and can be added to certain formulas of this invention at levels of from 3 to 8%. Alkali metal, preferably potassium or sodium, silicates having a weight ratio of  $\text{SiO}_2:\text{MgO}_2$  of from 1.0:1 to 2.8:1 can advantageously be used, where M in this ratio is the alkali metal. A sodium silicate having

a ratio of  $\text{SiO}_2:\text{Na}_2\text{O}$  of about 1.6:1 to 2.45:1 is especially preferred for economy and effectiveness.

In the embodiment of this invention which provides for a built liquid detergent, a hydrotropic agent at times is found desirable. Suitable hydrotropes are water-soluble alkali metal salts of toluene sulphonic acid, benzene sulphonic acid, and xylene sulphonic acid. The preferred hydrotropes are the potassium or sodium toluenesulfonates. The hydrotropic salt can be added, if desired, at levels of 1 to about 12%. While a hydrotrope will not ordinarily be found necessary, it can be added if so desired, for any reason including the preparation of a product which retains its homogeneity at a low temperature.

The term "coconut alkyl" as used herein and in the following examples refers to alkyl groups which are derived from the middle cut of coconut alcohol having the following approximate chain length distribution: 2%— $\text{C}_{10}$ , 66%— $\text{C}_{12}$ , 23%— $\text{C}_{14}$ , and 9%— $\text{C}_{16}$ . Other compounds designated as coconut oil derived are based on unfractionated coconut oil or its fatty acids.

The following examples are illustrative of several detergent compositions of this invention.

#### EXAMPLE I

A shampoo composition was prepared having the following composition:

	Parts by Weight
Sodium coconut alkyl glyceryl ether sulfonate (about 23% diglyceryl and the balance substantially monoglyceryl)	25.0
Sodium tallow alkyl glyceryl ether sulfonate (about 23% diglyceryl and the balance substantially monoglyceryl; the tallow alkyls correspond to those of substantially saturated tallow alcohols and contain approximately 2% $\text{C}_{14}$ , 32% $\text{C}_{16}$ and 66% $\text{C}_{18}$ )	3.0
Sodium chloride	6.7
Sodium sulfate	3.3
Sodium N-lauryl sarcosinate	3.8
N-coconut acyl sarcosine	1.2
Diethylanolamide of coconut fatty acids	2.0
Acetylated lanoline	1.0
Perfume	0.4
Color	0.04
3,4,4'-trichlorocarbaniide*	2.0
Polyethylenimine/ethylene oxide reaction product (weight ratio 1:1, molecular weight 80,000—120,000)	0.5
Water	Balance

\*Average particle size 2 microns

The 3,4,4'-trichlorocarbaniide and ethoxylated polyethylenimine were uniformly admixed and added to and uniformly mixed with the balance of the components. The resulting product was a stable cream having excellent cosmetic and antidandruff properties. The degree of deposition of 3,4,4'-trichlorocarbaniide from this composition was much greater than the degree of deposition attained with a similarly formulated product which contained no cationic polymer. Residual antimicrobial activity of surfaces washed with this composition is markedly greater as compared to surfaces washed with a control product without polymer.

Compositions identical to the composition of Example I, but containing 5 micron diameter particles of 3,4,4'-tribromosalicylanilide; 4,4' - dichloro - 3 - (trifluoromethyl)carbaniide; and bis(2 - hydroxy - 3,5,6 - trichlorophenyl)methane, and 6.5 micron particles of N - trichloromethylmercapto - 4 - cyclohexene - 1,2 - dicarboximide and N - (1,1,2,2 - tetrachloroethylsulfenyl) - cis -  $\Delta$  - 4 - cyclohexene - 1,2 - dicarboximide, respectively, in place of 3,4,4'-trichlorocarbaniide are prepared and compared with control compositions containing these compounds without cationic polymer. The degree of deposition and retention of these compounds in the presence of the cationic polymer is found to be substantially greater than is attached with the control compositions, and a corresponding increase in residual antimicrobial activity is observed on surfaces washed therewith.

#### EXAMPLE II

An antimicrobial milled toilet detergent bar which also constitutes a preferred embodiment of this invention is prepared in accordance with methods well known in the art and having the following composition:

	Parts by Weight
Sodium alkyl glyceryl ether sulfonate*	8.0
Potassium alkyl sulfate*	20.0
Magnesium soap of 80:20 tallow: coconut fatty acids	16.7
Sodium soap of 80:20 tallow: coconut fatty acids	32.4
Inorganic salts (sodium and potassium chloride and sulfates)	9.2
3,4,5-tribromosalicylanilide	1.0
(Average particle size 5 microns)	2.0
Polyethylenimine**	10.7
Water and miscellaneous	120

\*Alkyl groups derived from middle cut of alcohols obtained by catalytic reduction of coconut alcohol which has a chain length distribution substantially as follows: 2%— $\text{C}_{10}$ , 66%— $\text{C}_{12}$ , 23%— $\text{C}_{14}$ , and 9%— $\text{C}_{16}$ .

\*\*Molecular weight 50,000

The deposition and retention of the particulate antimicrobial agent 3,4',5 - tribromo - silicylanilide upon skin washed with the above composition is substantially greater than occurs with a control composition without cationic polymer.

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Toilet detergent bars identical in composition to the bar described above are prepared, replacing the 3,4',5 - tribromosalicylanilide with 4 micron particles of the antimicrobial agents 3,4,4' - trichlorocarbanilide; 4,4' - dichloro - 3 - (trifluoromethyl)carbanilide; bis(2 - hydroxy - 3,5,6 - trichlorophenyl) - methane; and a 1:1 mixture of 4,4'-dichloro-3 - (trifluoromethyl)carbanilide and 3,4',5 - tribromosalicylanilide, respectively, with improved deposition and retention of the antimicrobial particles being attained in each case relative to control compositions without polyethylenimine.

#### EXAMPLE III

An antimicrobial granular built laundry detergent product is prepared by conventional means, having the following composition:

	Parts by Weight
Sodium alkyl benzene sulfonate (the alkyl group averaging about 12 carbon atoms and being derived from polypropylene)	17.5
Sodium tripolyphosphate	49.7
Sodium sulfate	13.3
Silicate solids	7.0
3,4,4'-trichlorocarbanilide (particle size averaging 3 microns)	0.5
Polyethylenimine/ethylene oxide reaction product (weight ratio 4:1, molecular weight 50,000)	1.5

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Each of the foregoing Examples describe embodiments of this invention which involve antimicrobial particulate substances. As hereinbefore disclosed, the deposition and retention of other particulate substances are also enhanced by the cationic polymers. The following examples are illustrative of detergent compositions in accordance with this invention containing representative particulate substances which function through deposition and retention on washed surfaces.

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Toilet detergent bars desirably contain a sunscreen or ultraviolet absorber which will deposit on the skin in the course of washing therewith to provide protection against harmful sun rays. Suitable particulate ultraviolet absorbers which can be incorporated in detergent bars for this purpose are, for example, 2 - hydroxy - 4 - n - octoxybenzophenone, 2 - hydroxy - 4 - methoxy - 2 - carboxybenzophenone, and 2 - hydroxy - 4 - meth -

oxybenzophenone. These materials are insoluble particulate solids which are employed in bar soap formulations in concentrations ranging from about 1% to about 5% by weight.

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#### EXAMPLE IV

A toilet soap bar containing an ultraviolet absorber is formulated in accordance with this invention as follows:

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	Percent by Weight	
Sodium soap of 50:50 tallow: coconut fatty acids	73.19	75
Coconut fatty acid	7.30	
Cold cream	1.10	
Inorganic salts (sodium chloride and sulfonate and silicate solids)	0.87	80
Perfume	1.23	
2-Hydroxy-4-n-octoxybenzophenone (Particle size 10 microns)	2.50	
Cationic polymer*	3.00	85
Miscellaneous	0.81	
Water	10.00	

\*Polyethylenimine/ethylene oxide reaction product (weight ratio 4:1, molecular weight 50,000)

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When used in the customary fashion, the toilet soap bar of this Example effects a substantially greater degree of deposition and retention of the particulate ultraviolet absorber (2 - hydroxy - 4 - n - octoxybenzophenone) on the washed skin surfaces than does an identical composition without polymer.

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Additional toilet soap bars are prepared as above but containing 2-hydroxy-4-methoxy-2' - carboxybenzophenone and 2 - hydroxy - 4-methoxybenzophenone, respectively, in place of 2 - hydroxy - 4 - n - octoxybenzophenone, with substantially equivalent results.

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Other insoluble particulate substances which are desirably incorporated in toilet soap or detergent bars include the so-called "skin feel enhancers". Such materials are deposited as particles on the skin in the course of washing and create a favorable skin "feel" after washing. Such materials include, for example, nicotinic acid, talc and silicones, such as Dow-Corning Silicone F-157. These materials are desirably incorporated in a toilet bar formula at levels of about 10% by weight.

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#### EXAMPLE V

A bar soap formulation as set forth in Example IV is prepared substituting 9.8% by weight of nicotinic acid particles (average particle size 5 microns) for the 2-hydroxy-4-n-octoxybenzophenone and coconut fatty acid.

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The resulting composition yields a substantially greater degree of deposition and retention of nicotinic acid particles on skin washed with the bar than is attained with a bar similarly formulated but without cationic polymer. Similar results are obtained when Dow-Corning Silicone F-157 is used in place of nicotinic acid.

- 5 Various insoluble fabric whiteners or brighteners, such as fluorescent dyes and bluing, e.g., ultramarine blue, deposit as particles on fabrics washed with laundry detergent products containing same. Such materials can be used in heavy-duty laundry detergent products in concentrations up to about 1% by weight.

#### EXAMPLE VI

- 15 A built liquid detergent formulation containing a particulate bluing material and a cationic polymer in accordance with this invention is formulated as follows:

	Percent by Weight
25 3(N,N-dimethyl-N-coconut-ammonio)-2-hydroxypropane-1-sulfonate	9.00
Tergitol 12-P-12 (condensation product of 12 moles of ethylene oxide and one mole of dodecyl-phenol)	3.00
30 Tripotassium methylene diphosphate	26.00
Sodium silicate (SiO <sub>2</sub> :Na <sub>2</sub> O=1.6:1)	3.00
35 Potassium toluenesulfonate	8.50
Sodium carboxymethylhydroxyethylcellulose	0.30
40 Ultramarine blue (particle size 1.8 microns)	0.15
Cationic polymer (Same as Example I)	3.5
Water	Balance

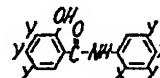
- 45 The above composition when used to launder white fabrics in the conventional methods results in the deposition and retention of substantially greater quantities of the ultramarine blue particles on the washed fabrics than occurs when a product similarly formulated but without cationic polymer is used.

- 50 It will be obvious to those skilled in the art that the concept of this invention is applicable to a wide variety of insoluble or sparingly soluble particulate substances in addition to those specifically described in the foregoing specification. For example, per-  
55 fumes which have been adsorbed on insoluble particulate resinous substances can be deposited on skin, fabrics and other surfaces washed with detergent compositions containing same to a substantially greater degree,

through the inclusion in said compositions of a cationic polymer as herein defined.

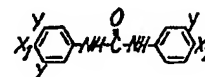
#### WHAT WE CLAIM IS:—

- 65 1. A detergent composition comprising:  
(1) an organic surfactant,  
(2) a water soluble cationic polymer which is a polyethylenimine having a molecular weight of 2,000 to 3,000,000 or a reaction product of polyethylenimine with ethylene oxide and/or propylene oxide the reaction product having molecular weight 30,000 to 1,000,000 and a weight ratio of polyethylenimine to alkylene oxide of at least 1:1,  
70 (3) a water-insoluble or sparingly soluble particulate substance, other than a heavy metal salt of 2-pyridinethiol-1-oxide, which is capable of imparting a desired residual property to a surface to which it becomes affixed when the surface is washed with the detergent composition.  
80 2. A detergent composition according to claim 1 in which the cationic polymer (2) is polyethylenimine of average molecular weight from 30,000 to 1,000,000.  
3. A detergent composition according to claim 1 in which the cationic polymer is ethoxylated polyethylenimine having molecular weight 80,000 to 120,000 and a weight ratio of polyethylenimine to ethylene oxide of at least 1:1.  
90 4. A detergent composition according to any of the preceding claims in which the water-insoluble or sparingly soluble particulate substance (3) is an antimicrobial agent which is a:  
95 (a) a substituted salicylanilide of the general formula:



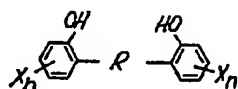
in which X is hydrogen or halogen and Y is hydrogen, halogen or trifluoromethyl,

- 105 (b) a substituted carbanilide of the general formula



in which Y is hydrogen, halogen or trifluoromethyl, X<sub>1</sub> is halogen or ethoxy and X<sub>2</sub> is hydrogen or halogen,

(c) a substituted bisphenol of the general formula



- 5 in which X is halogen and n is an integer from 1 to 3 and R is an alkylene radical having from 1 to 4 carbon atoms or is divalent sulphur,
- (d) N - trichloromethylmercapto - 4 - cyclohexene-1,2-dicarboximide,
- 10 (e) N - (1,1,2,2 - tetrachloroethylsulphenyl) - cis - Δ - 4 - cyclohexene - 1,2-dicarboximide; or
- (f) a mixture of two or more of the antimicrobial agents (a) to (e).
- 15 5. A detergent composition according to claim 4 in which the particulate substance is 3,4,4'-trichlorocarbanilide.
6. A detergent composition according to claim 4 in which the particulate substance is
- 20 3,4',5-tribromosalicylanilide.
7. A detergent composition according to claim 4 in which the particulate substance is 4,4'-dichloro-3-(trifluoromethyl)carbanilide.
- 25 8. A detergent composition according to claim 4 in which the particulate substance is bis(2-hydroxy-3,5,6-trichlorophenyl)methane.
9. A detergent composition according to claim 4 in which the antimicrobial agent is in admixture with a heavy metal salt of 2-pyridinethiol-1-oxide.
- 30 10. A detergent composition according to any of the claims 1 to 3 in which the particulate substance is a material which improves the feel of the skin when affixed thereto.
- 35 11. A detergent composition according to any of claims 1 to 3 in which the particulate substance is a fabric brightener.
12. A detergent composition according to
- 40 any of claims 1 to 3 in which the particulate substance is a substance which absorbs ultra violet light.
13. A detergent composition according to any of the preceding claims in which the particulate substance has an average particle diameter of from 0.2 to 50 microns.
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14. A detergent composition according to any of claims 4 to 11 in which the antimicrobial agent has a particle diameter of from 0.2 to 30 microns.

15. A detergent composition according to any of the preceding claims in which the organic detergent (1) is a water soluble salt of higher fatty acid, an anionic organic sulphonic reaction product having an alkyl group of from 8 to 20 carbon atoms and a sulphuric acid or sulphuric acid ester radical, or an acyl sarcosinate in which the acyl group has from 10 to 18 carbon atoms.

16. A detergent composition according to any of the preceding claims in which the detergent composition comprises from 2 to 95% by weight of the organic detergent (1) from 0.1 to 10% by weight of the water-soluble cationic polymer (2) and from 0.1 to 10% by weight of the water-insoluble or sparingly soluble particulate substance (3).

17. A detergent composition according to claim 16 comprising 0.25 to 4.0% by weight of the water-soluble cationic polymer and 0.5 to 2% by weight of antimicrobial agent.

18. A detergent composition according to any of claims 1—9 in which the organic surfactant (1) is at least one nonionic, ampholytic or zwitterionic surfactant and is present in an amount from 10% to 35% by weight, the cationic polymer (2) has molecular weight from 30,00 to 1,000,000 and is present in amount from 0.25% to 2.0% by weight; and the water-insoluble or sparingly soluble particulate substance is an antimicrobial agent and is present in amount from 0.5% to 2.0% by weight.

19. A detergent composition according to claim 1 in built liquid form which also contains a hydrotropic agent.

20. A detergent composition substantially as hereinbefore described with reference to the Examples.

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